

ON THE INTERRELATION OF SURFACE TENSION AND VISCOSITY FOR GLASS MELTS

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The interrelation of the surface tension and viscosity of glass melts is examined from the physical-chemical and technological standpoints. The corresponding relations and experimental results are presented. The interrelation of the surface tension and viscosity is also examined for technological processes: glassmaking, interaction of molten glass with refractories, formation of different types of glass articles, thermal polishing and edge melting of articles and foaming during the production of foam glass.

Key words: glass melts, surface tension, viscosity, technological processes, glassmaking, formation, foaming.

A technology can be developed and improved most effectively when the physical-chemical principles of the technological processes are known. As a rule, any heterogeneous process always starts from the surface and migrates into the interior volume. This is true of processes where physical factors predominate as well as processes involving chemical interactions.

Interrelation of Surface and Volume Characteristics.

A description of diverse interactions and phenomena occurring in liquids (solutions, melts) can be based on the obvious assertion that their main properties are a function of the state. This means that fundamental characteristics such as the viscosity, surface tension, density and others not only depend on the composition, temperature, pressure and other parameters but they are also interrelated. Surface phenomena and the interrelation of properties, including surface and volume properties, are examined in [1 – 4]. It should be noted that studies show a connection between surface tension and fundamental physical constants. Thus, equations relating the surface tension of single-component liquids with the following are obtained in [5] on the basis of dimensional analysis: a) the sound velocity in liquids and self-adsorption (specific compaction of matter in the surface layer); b) the atomic volume and Planck's constant.

The most characteristic and technologically important volume kinetic characteristic of liquids and especially silicate melts is the viscosity. The viscosity of glass is studied in many works, including works on calculations of viscosity as a function of temperature and composition. On the other

hand it should be noted that surface phenomena, which are studied in far fewer works than is viscosity, play an important role in the technology of glass. The role of transport and surface phenomena in glass technology is reflected in the reviews [6, 7]. At the same time the interrelation of viscosity and surface tension for glasses has not been adequately studied. For this reason we shall examine this interrelation from the physical-chemical standpoints as well as in application to a number of technological processes occurring in glass production.

PHYSICAL-CHEMICAL PRINCIPLES

The surface tension and viscosity are properties characteristic of liquids, including melts, and are associated with their structure. The structural particulars of glass melts are examined in [8]. According to the cluster model glass melts consist of micro-uniform regions (structural complexes) connected by interlayers, differing from the complexes by the character of the atomic interactions with the formation of weak and overstressed bonds. Since energy data show intercluster layers and boundary regions to be the weakest locations, it is precisely there that it is easiest for fluctuations of different kinds (chemical composition, temperature and others) to arise and different changes occur more quickly.

From the theoretical standpoint the relation between viscosity and surface tension must be quite complicated, because the structural particulars of the surface and interior volume are different; the character of the changes occurring in these properties as a result of thermal (temperature) and chemical (composition) changes is also different.

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The relation between surface tension and viscosity is evident in theoretical and empirical equations that include both quantities as a function of one and the same parameter, for example, density. The most reliable equation, checked on a large amount of experimental data, is A. I. Bachinskii's equation for the viscosity of liquids:

$$\eta = a/(V - w), \quad (1)$$

where V is the specific volume and a, w are constants.

Another well-known equation for the surface tension was derived for temperatures far enough from the critical temperature so that the vapor density can be neglected compared with the density of the liquid:

$$\sigma = B\rho^4, \quad (2)$$

where σ is the surface tension, B is a constant and ρ is the density.

Expressing the specific volume in terms of the density in Eq. (1)

$$a/\eta = V - w = (1/\rho) - w$$

and substituting the density from Eq. (2) we obtain

$$a/\eta = (B/\sigma)^{1/4} - w. \quad (3)$$

The relation between the surface tension and the viscosity has been examined by a number of authors (A. I. Bachinskii, S. Sagden, S. Bukhler, et al.) on the basis of the dependence of these properties on the structure of a given material. The molecular mass was taken as a structural characteristic. In this case the general form of the dependence of the surface tension and viscosity on the molecular mass M and density ρ is similar and characterized by the *parachor* P (for the surface tension)

$$P = M\sigma^{1/k}/\rho$$

and the *rheochor* R (for the viscosity)

$$R = M\eta^{1/b}/\rho. \quad (4)$$

S. Bukhler derived an equation which was used initially for a number of solutions of organic and polymer compounds:

$$\sigma^{1/4} = P(\log \log \eta + 2.9)/J = (\log \log \eta + 2.9)/K, \quad (5)$$

where J, K are constants determined from the experimental data.

The equation (5), expressing a quite complex interrelation of the surface tension and viscosity, does not have adequate theoretical validation and is not universal. At the same time this equation has been checked for a number of liquid (solutions and melts). Satisfactory results have been obtained for silicate glasses in the temperature range 1100 – 1400°C.

Other, more complicated relations reflecting the relation between the surface tension and viscosity have also been obtained [2].

Relaxation Phenomena. These phenomena are due to a transition from nonequilibrium to equilibrium states as a result of the displacement of kinetic units. For this reason these phenomena have a general nature for all processes: a system driven out of an equilibrium state strives to reach equilibrium at a rate proportional to the degree of deviation from equilibrium.

A relation between the surface tension and viscosity is also seen in relaxation phenomena, specifically, in the establishment of equilibrium values of the surface tension. The surface tension of multicomponent solutions and melts, reflecting the process leading to the formation of a new surface, varies in time from the moment it is formed. This is due to the following factors:

- the overcoming of the viscous resistance forces, which also impede the diffusion of surfactants;
- competing adsorption of the dissolved components and establishment of adsorption equilibrium on the surface;
- formation of the structure of the surface layer.

The surface tension and viscosity of paint (ink) are decisive for the technological processes occurring in printing. The efficiency of the equipment and the printing quality depend on their ratio. The change in the surface tension in time during the relaxation process is very important. This characteristic is called the dynamical surface tension, which can be determined by the method of the maximum pressure in a bubble. For high printing speeds and rapid drying of the printing ink on paper or other substrate equilibrium values of the surface tension are not reached in the technological printing process.

The kinetics of the variation of the surface tension polymer systems is studied in a number of works, which are generalized in the monograph [2]. The authors of one work, who considered the establishment of the equilibrium value of the surface tension to be an ordinary relaxation process, showed that this process can be satisfactorily described by the Kohlrausch equation:

$$\sigma_\tau - \sigma_e = (\sigma_0 - \sigma_e) \exp(-\tau/\tau^*), \quad (6)$$

where σ_0 , σ_τ and σ_e are the initial value of the surface tension, the value at the time τ and the equilibrium value, respectively; τ^* is the relaxation time.

Relaxation processes play an appreciable role for highly viscous glass melts. Basically, they are associated with structural changes and the operational reliability of glass articles (stress relaxation during annealing) and they can be described by the Kohlrausch equation. In regards to the ratio of the viscosity and surface tension it should be noted that viscosity plays a decisive role because of its high initial values and rapid growth with decreasing temperature. In this connection the relaxation time of the surface tension is quite

long, and in a number of technological processes the surface (interphase) tension takes on nonequilibrium values [9].

The action of surface forces is commensurate with the viscosity only for small objects; this will be shown in a subsequent article. Furthermore, there are practically no data on the surface tension of solid glass. The only work on determining the surface tension of solid glass is by V. P. Berdenikov, a quite detailed exposition of which is given in the monograph [10]. The results of measurements of the surface energy of glass in different liquids and in vacuum are presented. The values obtained range from 0.3 to 1.26 J/m². No other methods, described in, for example, the monograph [11], for studying the surface tension of glass were used. At the same time, in [12] it is noted that it is impossible to determine the surface tension of solids experimentally and it is recommended that the computational methods of [2] be used.

Particulars of Surface Convection. A liquid moves under the action of both volume (mass) and surface forces. The most common mass forces arise with a local change of the density of a liquid under gravity. The regularities of this form of convective motion have been studied quite well. The surface forces acting tangentially to the free or interphase surface of the liquid appear together with a nonuniformity of the surface tension and tend to increase it [13]. Drawing the surface and the adjoining layers of the liquid into motion these forces initiate the development of volume convective motion, whose intensity increases with decreasing thickness of the layer (Marangoni effect, Marangoni convection). Such phenomena are characterized by the Marangoni number:

$$Ma = \Delta\sigma L / \eta D, \quad (7)$$

where $\Delta\sigma$ is the gradient of the surface (interphase) tension, L is a characteristic length, η is the viscosity and D is the diffusion coefficient.

It follows from the expression (7) that the character of the fluid motion occurring under the action of surface forces is directly related to the main kinetic characteristics at the interphase boundary — the viscosity and rate of mass transfer.

The simplest and most common reason for the formation of a nonuniform distribution of the surface tension is the temperature dependence of σ . For most liquids, including melts, σ decreases linearly with increasing temperature, so that the motion of the liquid along the surface is directed toward the colder region. Such Marangoni convection, usually referred to as thermocapillary convection, inevitably arises in nonuniformly heated multiphase systems with an interface between phases (or with a free surface between a liquid and gas) and can make a large contribution to heat and mass transfer processes in these media.

The surface tension varies not only with temperature but also in the presence of surfactants (S). Ordinarily, the surface tension in multicomponent liquids depends on their composition. This dependence is determined by the nature and physi-

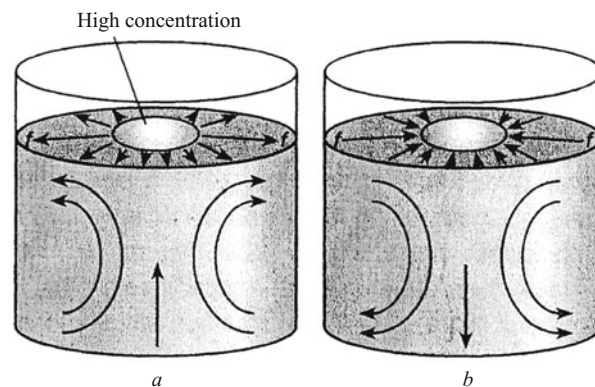


Fig. 1. Scheme of Marangoni concentration-capillary convection on the surface and in lower-lying layers of the liquid: a) $\partial\sigma/\partial C < 0$; b) $\partial\sigma/\partial C > 0$.

cal-chemical properties of the components and can be nonlinear. For this reason the nonuniform distribution of the components, especially surfactants in solution or melt, results in the development of concentration-capillary convection. The surface tension decreases with increasing concentration C of the surfactant; the surface forces will be directed along the surface of the liquid and will strive to increase the area of the region with a high concentration of the surfactant. If σ increases with increasing concentration of a component, then, conversely, the forces arising strive to decrease the area. In this way the surface forces give rise to motion of the surface and near-surface layers of the liquid. The viscous resistance of these and lower-lying layers will cause deeper layers, where convective motion arises, to be drawn into the motion. The total thickness of the convective layer of liquid is comparatively small, but nevertheless the near-surface mass transfer is much more intense than diffusion. A diagram of Marangoni concentration-capillary convection is shown in Fig. 1.

The surface tension σ decreases for the surface layer of a liquid with an adsorbed surfactant. If some element of the liquid from deep layers rises to the surface under the influence of fluctuations and perturbations, then a section with a relatively low concentration of the surfactant and, therefore, higher surface tension appears at this location on the surface. In the process surface forces directed radially toward this section arise and displace this section off the surface into the interior volume.

Marangoni convection also strongly affects the flow of many technological processes in the food, chemical, metallurgical and silicate (including glass) industries. Specifically, the Marangoni effect appears in the technological processes occurring in glassmaking, the interaction of molten glass with refractories, and the production of microspheres and foam glass. The particulars of thermo- and concentration-capillary convection are presented in [14, 15].

Kinetic Relations. The kinetics of the processes occurring under the action of surface forces in a high-viscosity

medium is determined by the viscous resistance of the medium and other factors associated with relaxation phenomena. These factors determine the appearance of nonequilibrium values of the surface (interphase) tension in the course of a technological process. In this case viscosity plays the main role, because all other factors are associated with it in one way or another.

To determine the role of the viscous resistance of a medium (molten glass) it is convenient to analyze the factors arising when a drop or bubble is squeezed through a tube with a sufficiently small diameter (determination of the surface tension by the method of maximum pressure in a drop or bubble).

In determining the surface tension by this method the pressure is expended on overcoming the surface-tension force P_σ and viscous resistance force P_η :

$$P_{\max} = P_\sigma + P_\eta. \quad (8)$$

For small objects the action of surface forces is associated with the formation and movement of spherical surfaces. In the process of slow formation of a spherical bubble or drop under the action of gradually increasing pressure the viscous resistance force will be proportional to the radius of the sphere, the velocity of the sphere and the viscosity of the medium (molten glass) in accordance with Stokes' law

$$F = Arv\eta, \quad (9)$$

where A is the coefficient of proportionality, r is the radius of the moving sphere, v is the velocity of the sphere and η is the viscosity of the molten glass.

Taking account of the uniform motion of the sphere toward the cut-off of the tube the velocity can be represented as $v = r/\tau$. Taking this into account and referring the force to unit area we have

$$P_\eta = A\eta/g\pi\tau = A^* \eta/\tau, \quad (10)$$

where τ is the time, g is the acceleration of gravity and A, A^* are constants.

The pressure expended on overcoming the surface tension is

$$P_\sigma = 2\sigma/rg = B^* \sigma/r, \quad (11)$$

where B^* is the coefficient of proportionality.

Over a sufficiently long time the effect of the viscous resistance of the medium practically vanishes; this is used in maximum-pressure methods in accordance with the relation (8). Conversely, in the case of brief actions the viscous resistance forces play the dominant role. In a number of technological processes in glass production gravity also has an effect and in order to determine the rate of a process the relation between the main acting forces must be taken into account. For this reason the following relation, which takes ac-

count of the force of gravity P_g , is introduced in addition to the relations (9) and (10):

$$P_g = C^* m/s, \quad (12)$$

where C^* is a coefficient of proportionality, m is the mass of the molten glass (article) and s is the cross-sectional area.

Comparing the relations (10) – (12) reveals the statistical character of the surface forces, the force of gravity and the kinetic character of the viscous resistance. If the surface forces and the force of gravity are expended on overcoming the viscous resistance of the molten glass, then the duration of the process can be estimated from the relations

$$\tau_\sigma = K^* r \eta/\sigma; \quad (13a)$$

$$\tau_g = Ms\eta/m, \quad (13b)$$

where K^* and M are coefficients.

The kinetic coefficients (12) – (13) characterize the technological interrelation of the viscosity, surface tension and gravity and can be used to analyze and evaluate the factors involved in the formation of sheet glass on tin melt, small toroidal articles (beads), glass microspheres and the appearance and motion of particles of one phase inside another phase toward phenomena occurring when the glass in articles partially melts (thermal polishing of the surface, gas-flame processing of electric lamps, household articles and others).

TECHNOLOGICAL PROCESSES

We shall now look at examples of technological processes where the result is a consequence of the manifestation of the interrelation of the surface tension and viscosity of glass.

Glassmaking. In a glass furnace after silicate and glass formation has stopped the surface layer of the molten glass in contact with a gas medium is very nonuniform. Mobile sections with different composition, viscosity and surface tension are present on the surface. The character of the motion under the action of surface forces was studied using model liquids [16]. Vortex motion of low-viscosity model liquids under the action surface forces was found. Of course, intense vortical motion is impossible in high-viscosity glass melts, but considerable movements on interphase boundaries will occur. Surface tension gradients lead to the appearance of Marangoni convection (see Fig. 1) and quite intense mass transfer in near-surface layers, greatly surpassing diffusion mass transfer and promoting homogenization of the molten glass. Furthermore, it is necessary to take account of the nonequilibrium character of the surface and interphase tension in high-viscosity melts. The data from experiments and industrial observations of mass transfer processes occurring under the action of surface forces are very interesting. For example, sections with high surface tension present on the surface of molten glass will be displaced into the interior of the melt while the interior layers will emerge onto the surface. In addition, such mass transfer can occur when local

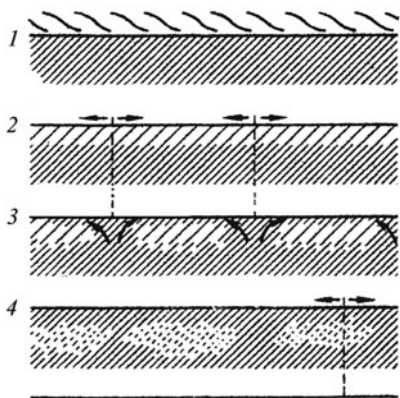


Fig. 2. Scheme of surface mass transfer in a glass furnace, occurring under the influence of changes in the surface tension: 1) initial surface of the molten glass; 2) discontinuity of the surface layer accompanying a change in the surface tension; 3) rise of lower-lying layers to the surface of the molten glass; 4) displacement of the surface layers into the interior of the molten glass.

conditions on the surface of molten glass change and 'discontinuities' form in the surface layer (Fig. 2).

Interaction of Molten Glass with Refractories. The main factors of this interaction are the chemical interaction of molten glass with refractories and the action of surface forces. The maximum breakdown refractories at the level of the free surface of the molten glass is due to intensified motion of molten glass at phase interfaces (convection in the boundary layer) with increasing surface and interphase tension in the contact layer owing to increased Al_2O_3 and ZrO_2 content in this layer. The Marangoni effect is also manifested. The active convection of molten glass in the surface and boundary layers in turn decreases the thickness of the boundary layer, increases the rate of mass transfer and intensifies the breakdown of refractories. A schematic diagram of the mechanism of breakdown of girders at the level of the free surface of the molten glass is presented in Fig. 3. Wetting and drop formation processes play a significant role. They are practically wholly determined by chemical interaction and the action of surface forces, in turn dependent on the viscosity, which ultimately determines the rate of the technological process. These processes are similar to those occurring with the participation of low-viscosity liquids taking account of the difference of their viscosity. In addition, if the velocity of the surface flow for water solutions is of the order of 10^{-2} m/sec, then this velocity will be many times lower for glass melts in accordance the ratio of the viscosities.

Surface phenomena also play a decisive role in vertical cellular corrosion due to gas bubbles. The changes in the surface and interphase tension at phase interfaces and the Marangoni effect result in rotational and reciprocating motion of bubbles with continual renewal of the interface. Such action of the surface forces promotes accelerated chemical interaction and mass transfer, giving a comparatively high rate of the vertical cellular corrosion. The results of investi-

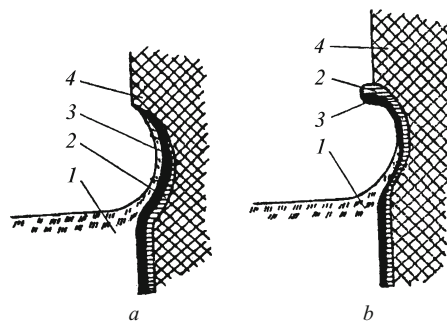


Fig. 3. Scheme of the breakdown of refractory girders at the level of the free surface of the molten glass (according to I. Lefler): a) process start; b) drop formation and detachment; 1) glass with the initial composition; 2) near-contact glass; 3) alkali oxide depleted glass; 4) refractory.

gations of the interaction of refractories with molten glass during melting are systematized in the reviews [16, 17].

However, it should be noted that under the practical conditions of glassmaking the quality of the refractories and their cooling at the level of the free surface of the molten glass are decisive for increasing the viscosity and decreasing the diffusion characteristics in order to slow down mass transfer in the contact layers. The factor reducing the reactivity of molten glass by decreasing the content of active components in the glass can be used up to a certain limit. At the same time the factor reducing the gradient of the interphase tension in the contact layers is used when the refractories are made of chromium oxide, in which high resistance is combined with the surface activity of chromium oxides.

The **formation of glass articles** is possible under isothermal and non-isothermal conditions. The formation under isothermal conditions occurs at constant temperature (formation of sheet glass on tin melt, small spheroidal articles). In this case the shape of the article is formed when surface forces combine with gravity followed by cooling and solidification of the glass.

In the case of formation under non-isothermal conditions articles are formed under the action of external forces (extrusion, rolling, pressing, blowing out and others) with bounding devices (rollers, molds and others) being used while the glass is hardening. In this case the smoothing of small nonuniformities of the surface in a thin layer and the rounding of the edge zones limit the action of the surface forces.

Formation of sheet glass on tin melt. In the float process the molten glass spreads on the tin melt under gravity and $P_g \gg P_\sigma$. However, surface forces limit the spreading right up to the formation of a lens with a definite equilibrium thickness given by

$$h = \sqrt{\frac{2L\rho_t}{g\rho_{mg}(\rho_t - \rho_{mg})}}, \quad (14)$$

where h is the thickness of the glass lens; $L = \sigma_{mg} + \sigma_{ip} - \sigma_t$ is the spreading factor; ρ_t and σ_t are the density and surface

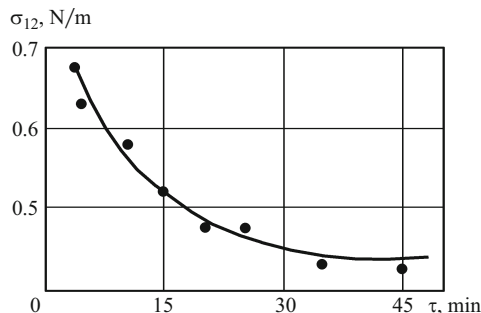


Fig. 4. Kinetics of the variation of the interphase tension on the glass – tin boundary at 1200°C.

tension of tin; ρ_{mg} and σ_{mg} are the density and surface tension of the molten glass; and, σ_{ip} is the interphase tension.

High values of the viscosity of molten glass and the kinetic character of the viscous resistance forces lead to the appearance of nonequilibrium values of the surface and interphase tension. Figure 4 shows the change in the interphase tension in the glass – tin system at 1200°C (the method of x-ray photography of a tin drop in the molten glass). Glass with following compositions was used for the experiments (wt.%): laboratory made (SiO_2 — 75, CaO — 10, Na_2O — 15) and commercial (SiO_2 — 71.8, Al_2O_3 — 2.0, Fe_2O_3 — 0.1, CaO — 8.6, MgO — 3.6, Na_2O — 13.6, SO_3 — 0.3).

Values of the interphase tension above the equilibrium values are observed for contact times less than required to overcome the viscous resistance forces on an interphase boundary. Such values are also observed under practical conditions in the float process. Ordinarily, the thickness of a glass lens or ribbon is considered to be an equilibrium value. However, analysis of the relation (14) shows that such a thickness is obtained because the interphase tension exceeds its equilibrium values. This is associated with the high viscosity of the molten glass and the limited residence time of the molten glass in the formation zone of a layer of equilibrium thickness. Thus, for the float process it is more accurate to characterize the glass lens or ribbon thickness as a *technologically equilibrium quantity*.

Formation of glass fibers. As noted above the technological interrelation of the surface tension and viscosity is most strongly manifested for small articles. When thin fibers are drawn from solutions and melts, including glass melts, the critical length l of a ‘liquid’ filament is determined by the following generalized equation [18]:

$$l = v\tau = kvr\eta/\sigma \quad (15)$$

where v is the drawing rate of the filament; τ is the time; k is a proportionality coefficient; r is the radius of the filament; and, η and σ are, respectively, the viscosity and surface tension of the liquid (solution, melt).

The ratio η/σ appearing in the relation characterizes the fiber-forming capacity of the liquid and can be used to deter-

mine the production capacity of glasses used in the production of glass fibers [19]. But viscosity plays the decisive role here, since its dependence on the composition and especially the temperature is incomparably greater than on the surface tension. For example, for quartz-glass melt $\eta/\sigma \gg 1000$ and this ratio more than 10 times greater than the analogous ratio for a melt of nonalkaline aluminum-boron-silicate glass E. For glass melts with different chemical composition used to obtain high-modulus, aluminum-silicate, semiconducting, protection and other fibers this index is less than 100.

Even though its effect on the glass production capacity is weaker than that of viscosity, the surface tension promotes the formation of an almost defect-free fiber surface, which in combination with rapid cooling and ‘freezing’ of the high-temperature structure gives high-strength continuous glass fibers.

Staple is also formed by means of external forces (centrifugal forces, blowing energy) in combination with the action of surface forces. In this case the viscosity and surface tension of the molten glass must be relatively low [19].

Free formation of small spheroidal articles. Here it is necessary to distinguish two types of articles:

- glass microspheres (microballs — GMB and hollow microspheres — HMS)
- toroidal articles (beads).

The methods to produce such articles (0.05 – 3.00 mm) are based entirely on the action of surface forces. There are three methods for forming microspheres:

- ‘fragmenting’ a thin stream of melt (GMB);
- fusing particles of glass powder (GMB); formation and growth of an internal gas bubble (HMS);
- sol-gel technology:
 - a) drop method (microspheres are formed from a colloidal water solution of the components);
 - b) frit method (microspheres are formed from a solid xerogel of the appropriate fraction).

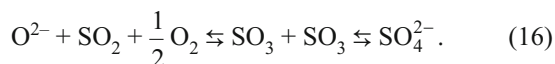
Formation of microspheres. To obtain comparatively large GMB from melt a thin stream of molten glass is ‘fragmented’ into discrete drops under the action of centrifugal forces or a gas stream with the formation process completed in an oven.

Most GMB, especially small ones, are produced by melting pre-ground glass in the gas-burner flames. Particles of arbitrary shapes are transformed into spherical particles under the action of surface tension forces which overcome viscous resistance forces. The duration and rate of the process can be evaluated by means of the relation (13a). Here it is necessary to take account of the fact that the surface tension exceeds the equilibrium values and accelerates the formation process.

In the case of the production of HMS from glass powder the driving force for the transformation of the solid glass particles into hollow microspheres is thermal dissociation of oxygen compounds of sulfur, which are dissolved in glass, at temperature above 1000°C to a definite degree of supersaturation. The sulfur compounds form and dissolve in glass

when the sulfates (usually Na_2SO_4) which are introduced into the batch during the melting process decompose. There is a great deal of research devoted to different aspects of the dissolution of sulfur oxides in glass. This work is systematized in [16].

The formation and dissociation of oxygen compounds of sulfur in glass proceed in accordance with the reaction



This equation relates the processes of formation in glass and release from the glass of the oxygen compounds of sulfur. The reversibility sign in this case is used as a generalized characteristic of the processes occurring during glassmaking and formation of microspheres. The conditions created must permit the process to go to the right in the first case and to the left in the case of hollow microspheres. The most important parameters according to Eq. (16) are the temperature, the redox conditions (the oxygen partial pressure in the furnace atmosphere and the activity of the oxygen ions in the melt) and the chemical composition of the glass. The process resulting in the formation of hollow microspheres usually proceeds with forced delivery of the initial glass micropowders into a gas stream heated to high temperature in the range 1000–1400°C (for example, the flame of a gas-air burner). In this case the gases (SO_2 and O_2) dissolved in the glass are released in each micropowder particle, and a microbubble appears and grows to a definite size, forming a hollow microsphere.

A bubble starts to form in the interior volume of a homogeneous liquid when an energy barrier equal to the formation energy of a bubble embryo with radius r and surface tension σ of the liquid is overcome:

$$W = 4/3\pi r^2 \sigma. \quad (17)$$

The nucleation of a bubble in a particle of micro-nonuniform glass is associated with the structural particulars of glass melt, which are examined in [8] and were noted above. The zones of preferred nucleation of bubbles form in energetically weaker locations (intercluster layers and boundary regions). Different kinds of fluctuations (chemical composition, temperature, gas-content and others) arise in these zones more easily. Microvoids transform under the action of gas pressure and surface tension into spherical bubble embryos capable of further growth. At the initial stage of growth the pressure in a bubble reaches a significant magnitude sufficient to overcome the viscous resistance forces. As a bubble grows the pressure in it drops and approaches the pressure of the surrounding medium. At the final stage of growth the pressure inside the bubble is balanced by the surface forces acting on the inner and outer surfaces of the microsphere and viscous resistance forces. Thus, the surface forces wholly form the microspheres on the inside and outside. The rate of acquisition of the spherical shape is deter-

mined by the temperature and the corresponding viscosity of the glass in accordance with the relation (13a). The technological process of obtaining GMB and HMS as well as their properties and application are reflected in [20–21].

Promising work on hydrogen energy is based on the use of HMS as micro-containers for storing the hydrogen to be used in engines, in laser-driven fusion and so forth. The formation of HMS by the drop method in sol-gel technology makes it possible to obtain HMS with more uniform sizes and has certain characteristic features [22, 23]. The technological process leading to the formation of HMS (about 150 μm) can be conducted in an approximately 5 m high vertical tubular gradient furnace. Hollow microspheres form during the fall of drops and subsequent passage through a furnace with different temperature. It should be noted that the HMS formation time in the furnace is about 5–10 sec, so that the rate of the processes in the corresponding zones of the furnace is quite high. In addition, the Marangoni and Gibbs effects appear rapidly and on microscales.

Physical-Chemical Processes in the Furnace Zones:

zone 1: production of drops (about 200 μm) of a water solution of glass-forming components in a drop generator;

zone 2: drop inflow \rightarrow evaporation of water from the surface \rightarrow formation of capsules with an elastic gel film on the surface (about 200 μm) and nucleated bubbles in the interior volume;

zone 3: formation of an inner cavity by merging of bubbles \rightarrow slowing of water evaporation and capsule growth (about 500 μm) by increasing water vapor pressure inside a capsule; this is the longest zone, and at the end of the zone the capsule size increases to about 1000 μm ;

zone 4: glass and HMS formation \rightarrow start of HSM size reduction under the action of the surface tension of the glass (about 300 μm);

zone 5: continuation of HMS size reduction \rightarrow attainment of equilibrium between the forces of the residual internal water vapor pressure, viscous resistance of the shell and surface tension of the glass \rightarrow equalization of the wall thickness, final spheroidization (HMS of fixed size (about 150 μm) and quality);

zone 6: collection of ready microspheres (about 150 μm).

Formation of toroidal articles (beads) on a substrate.

The articles were made from prepared tubular blanks with inner diameter 1 mm and height equal to the outer diameter ($d = h = 2.2$ mm) using glass with the following composition (wt.%): SiO_2 — 66.5; B_2O_3 — 2.2; Al_2O_3 — 2.7; CaO — 7.1; ZnO — 7.1; Na_2O — 14.0; Fe_2O_3 — 0.3; SO_3 — 0.2. The free formation of articles was conducted using a special burner apparatus which developed temperatures to 1200°C. A soot packing was used to prevent the central opening from being melted shut. The data on the temperature zones of the burner apparatus and on the change in shape of the articles on heating were obtained by the shadow method.

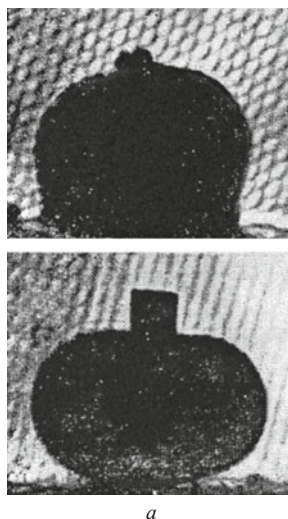
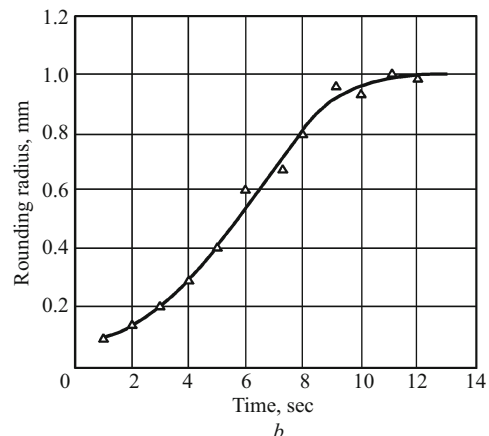


Fig. 5. Kinetics of the formation of toroidal articles on a substrate: *a*) final stages of formation of the articles; *b*) kinetics of the variation of the radius of the edge zones during the process.



The final stages of the formation of the articles are presented in Fig. 5a. The final shape of an article is result of the combined action of gravity and surface tension. The formation time or rate of the process is determined by the viscosity (13a). The protrusion in the upper part of the article comprises a residue of the soot packing, obtained as a result of the change in the shape and decrease in the height of the article.

The ratio of the surface forces and the force of gravity is expressed by the relation

$$\frac{P_{\sigma}}{P_g} = \frac{2\sigma\pi(R^2 - r^2)}{rgm}, \quad (18)$$

where R and r are, respectively, the outer and inner radii of the article.

The calculations give $P_{\sigma}/P_g = 13.5$. Thus, the toroidal shape of the article is formed when the surface forces predominate. The possible deviations of this shape are associated with the geometry of the blanks, the nonuniformity of the heat flux and other factors. The process time and rate are determined by the combined action of gravity and the viscous resistance in accordance with the relations (13).

The formation kinetics of the articles was also studied. The rounding radius of the edge zones, which was measured in a MIN-6 microscope equipped with a measuring eyepiece, was chosen as a criterion of the formation process. The temperature in the formation zone was 1200°C. The kinetic change of the radius of the edge zones of articles in the formation process is presented in Fig. 5b. The behavior of the curve shows that the blank is heated through during the first 5 sec of heat treatment, and the edges of the blank start to fuse under the action of surface tension. With subsequent heating of the blank and reduction of the viscosity of the glass the surface tension, overcoming gravity and the viscous resistance of the glass melt, deforms the blank and the radius of its edge zones increases, which is also seen in Fig. 5a. Subsequently, the curve reaches a plateau with constant radius, which attests to the completion of the formation process.

Thermal Polishing of the Surface and Edge Fusion of Glass Articles. The process of *thermal polishing*, for example, of the surface and edges of pressed articles after formation and ground figures on lead-crystal articles, can be conducted by means of convective and radiant action in the 'thermal shock' regime. Here, a thin surface layer of the glass must be heated and melted without the article becoming deformed. The smoothing of the rough surface is due to surface tension forces, which overcome the viscous resistance of the glass melt.

The rough surface of the glass after grinding can be represented in the form of alternating peaks and troughs. Then, the melting process and smoothing of the surface can be represented by a combination of processes leading to the formation of microspheres and spreading of the melt over the surface of the glass [24]. Here, the spreading process will be determined by the practically ideal wetting of the substrate by the melt formed.

Edge melting of glass articles is done during mechanized and manual production of press-blown and blown household glassware. For press-blown articles the 'hot' separation of the bubble cap is done immediately after formation using high-temperature gas burners, after which the articles are annealed. In the process a spherical thickening is formed on the edge of the article under the action of surface tension. For manually produced thin-wall articles the 'cold' separation of the bubble cap is done after annealing, after which the edge of the articles is fused; for some types of articles the edge is ground after the bubble cap is separated and before melting. During the thermal action a thin surface layer melts on the edge of the article; under the action of surface tension the melt moves along the solid substrate, smoothing (polishing) the ground surface on the flat face of the edge and rounding off the sharp edges.

To determine the technological interrelation of the surface tension and the viscosity of the glass the relation (13a) was checked during melting of the edge of 1.16 mm thick articles made of commercial glass with the following composi-

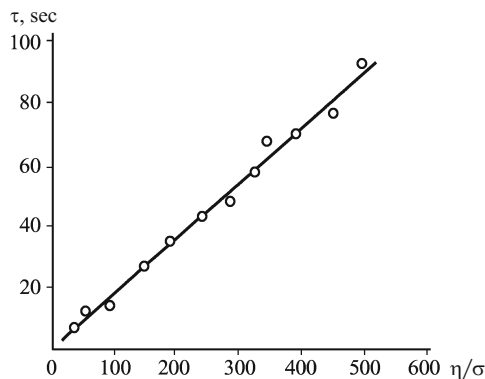
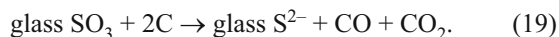


Fig. 6. Effect of the ratio η/σ on the completion time of the process during edge melting of articles.

tion (wt.%): SiO_2 — 74.5, CaO — 6.5, MgO — 2.5, K_2O — 2.5, Na_2O — 13.5, R_2O_3 — 0.5 and SO_3 — 0.5. The temperature dependences of the viscosity and surface tension were determined for this glass in the temperature interval 900 – 1200°C. A burner with stabilized heat flux, ensuring the stability of the temperature regime of melting within 3°C, was used for the experiments. The edge melting of the article at certain temperatures in the interval indicated above made it possible to determine the temperature dependence of the formation time of the spherical surface on the ratio η/σ (Fig. 6). It should be noted that the slope of the straight line $k = 0.18$ is close to the value of $3r$ in the relation (13a), which makes possible a kinetic evaluation of the processes occurring under the action of surface forces.

Foaming during Foam Glass Production. Foam glass is produced commercially primarily by the powder method. The essence of this method is as follows: the batch, consisting of ground glass and a foaming agent (0.5 – 3% of the glass by weight), is poured into a mold, heated to the temperature of active foaming, kept at this temperature for a definite period of time and then sharply cooled to stop gas formation, stabilize the foam structure and anneal the foam. The technological processes involved in the production of foam glass and their particulars are examined in [25 – 27].

During heating the glass particles first soften and then merge (sinter). For most glasses this occurs at temperature about 550 – 650°C. The viscosity of the nonuniform mass at these temperatures is high. On subsequent heating (about 750 – 905°C) the viscosity decreases and the chemical interaction with the molten glass and the foaming agent and its decomposition start. The generalized scheme of foaming for carbon foaming agents can be represented as follows [23]:



The released gases form in the molten glass spherical cavities (bubbles) on the boundaries of the nonuniformities (previously — *formation of microspheres*) and on the particles of the solid foaming agent. As the chemical interaction develops in accordance with the reaction (19) the diameter of

these bubbles gradually increases, and at the same time the bubbles come into contact with one another, form foam with polyhedral structure and the volume of the molten glass increases significantly.

The foam glass obtained by the powder method has much in common with foaming liquids. In both cases a coarsely disperse system, whose disperse phase (gas) is distributed in the dispersion medium (molten glass) whose volume is smaller. Dependences which are associated with the surface tension and the viscosity are characteristic for such systems.

The particulars of surface convection, which are associated with the manifestation of the Marangoni effect, were examined above. In foam systems this effect is manifested together with the Gibbs effect. These effects are associated with the stability of the foam bubbles, which is due to the surface tension, elasticity and viscosity of the bubble film.

In order to withstand the local deformations without rupturing the films must be capable of increasing the surface tension in the case of local stretching and decrease it during local compression. Any stretching of the bubble wall during a rise in pressure and temperature will increase the surface area of the bubble and, correspondingly, the surface tension.

An increase of the surface area is always accompanied by an increase of the free energy:

$$\Delta F = \sigma \Delta S + (S + \Delta S) \Delta \sigma. \quad (20)$$

where $\sigma \Delta S$ is the increase of the free energy of the surface and $(S + \Delta S) \Delta \sigma$ is the change in the free energy corresponding to the increase in the surface tension.

Gibbs established a relation between the last term of this equality and the surface elasticity of a film. In this connection, according to Gibbs the stability of the foam can be characterized by the modulus of surface elasticity:

$$E = 2S(d\sigma/dS). \quad (21)$$

For $E > 0$ the film is stable against local perturbations, because the elastic forces can prevent the destructive action of the perturbations and return the film into the initial state.

Thus, a bubble film possesses a definite elasticity together with thermo-capillary and concentration-capillary motion of liquid in the surface layer.

During foaming the gas pressure in the bubbles is expended on overcoming the forces of surface tension and viscous resistance of the molten glass in accordance with the relations (8) – (11):

$$P = P_\sigma + P_\eta = B^* \sigma/r + A^* \eta/\tau. \quad (22)$$

Foaming of glass melt occurs all the more easily the lower its surface tension. This is accomplished by introducing oxidizers (SO_3 , As_2O_3 , Sb_2O_3 and others) into the glass, which not only increase the oxygen potential of the glass, required to oxidize carbon, but they also possess surface activity. The foaming process must be smooth and gradual,

which is secured by the corresponding technological parameters, first and foremost, the viscosity, which can be regulated by means of the composition of the glass and the temperature regime of foaming. The viscosity of the molten glass during foaming is high enough to ensure that the foaming process is even and gradual. In addition, the quite high viscosity of the molten glass plays a stabilizing role, since it makes it possible to obtain comparatively thick bubble films and correspondingly slow down the motion of the molten glass in foam films under the influence of surface tension gradients and the force of gravity, thereby making the foam formed quite strong.

The questions examined in this article reflect a general trend in the study of the interrelation of surface and volume characteristic of liquids, melts and solids. Theoretical and phenomenological approaches making it possible to find more accurate relations are being developed. The development of these directions in the physical chemistry and technology of glass will make it possible to improve existing and develop new technological processes.

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